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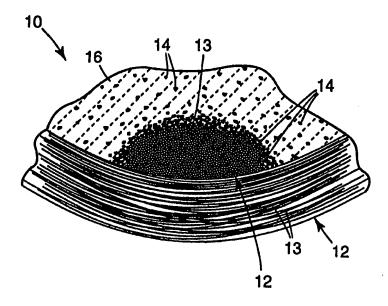
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(54) Title: TOUGH, LOW PERMEABLE CERAMIC COMPOSITE MATERIAL

(57) Abstract

Ceramic composite material comprising: a ceramic matrix comprising ceramic particles dispersed within a ceramic bonding phase; and a plurality of ceramic fiber bundles, each comprising a plurality of continuous ceramic fibers; wherein the ceramic matrix does not completely infiltrate a majority of the individual fiber bundles, and wherein the ceramic particles have at least one fraction of particles with a median particle size at least as large as the diameter of the largest individual fibers.

TOUGH, LOW PERMEABLE CERAMIC COMPOSITE MATERIAL

Field of the Invention

5   The present invention relates to ceramic composite materials, particularly to those containing a ceramic matrix reinforced with continuous ceramic oxide fiber bundles.

Background of the Invention

10   Use of ceramic materials in the form of articles that withstand high temperatures (e.g., furnace components) is frequently desirable due to their relative light weight and strength at high temperatures, as well as due to their relative chemical resistance. In general, however, ceramic materials tend to be brittle. Further, monolithic ceramic articles and structures (i.e., ceramic materials without reinforcement) tend to be

15   undesirably brittle, to be very sensitive to flaws, and to exhibit unpredictable catastrophic failure.

          Attempts to overcome these deficiencies include incorporating continuous fibers (e.g., ceramic fibers) into (brittle) ceramic material. Such constructions have been shown to result in relatively tough, fracture resistant, ceramic matrix composites. It is

20   believed that such constructions can result in the tough, fracture resistant, ceramic matrix composite if the fibers are able to span cracks as the cracks are formed or grow. In spanning a crack, the fibers continue to support at least some of the load across the crack, which then limits the strain at the tip of the crack. In order for this to happen, it is believed that the fibers need to move independently of the matrix at stress levels

25   below the fracture stress of the fibers. That is, such fibers are not particularly effective at preventing cracks in ceramic matrix composites where there is a strong bond between the fibers and the matrix. Such behavior may be attributed to the extremely high strain concentration existing at the tip of a brittle crack in the matrix, and that the stress developed at such a strain concentration is high enough to fracture an individual

30   reinforcing fiber. As each individual fiber is fractured, the load is transferred to the next fiber, and the fracture process is repeated sequentially until the crack has

progressed across the entire section. By contrast, however, it is believed that if the

bond between the reinforcing fibers and the matrix is slightly weaker (or nonexistent),

the concentrated load at a crack tip causes localized separation of the fiber from the

matrix, allowing the fiber to deform elastically (as by stretching) or mechanically (as by

5   untwisting) over a somewhat greater portion of its length, simultaneously transferring a

portion of the load to adjacent fibers.

Thus, approaches have been developed to produce ceramic composites that do

not possess a strong bonding interaction between the fibers and the matrix. In one

approach, the reinforcing fibers are coated with carbonaceous materials, for example, to

10   prevent strong bonding between the fibers and the matrix material. See, for example,

U.S. Pat. Nos. 4,935,387 (Bealle et al.), 4,935,235 (Heany), 4,397,901 (Warren), and

5,275,984 (Carpenter). This approach has not proven to be completely satisfactory,

however, because it has been difficult to find inexpensive fiber coatings that are stable

at high temperatures and/or under oxidizing conditions.

15   An alternative approach has been to form a matrix with a controlled amount of

porosity as disclosed, for example, in U.S. Pat. No. 5,488,017 (Szweda et al.). This

particular approach is designed to limit the strength of the bond between the fibers and

the matrix. Unfortunately, however, this approach also adds porosity to the matrix and

limits the toughness of the matrix.

20   Yet another approach has been to deposit the matrix material on continuous

ceramic oxide fiber bundles using chemical vapor deposition in a manner that does not

cause the matrix material to completely infiltrate the fiber bundles. This can be done by

limiting the diffusion of the vapor into the interior of each bundle. For example, silicon

carbide has been coated onto continuous aluminosilicate fiber bundles using chemical

25   vapor deposition. Although this method can provide a tough ceramic composite, it is a

very expensive. Furthermore, the composites are typically permeable to air at room

temperature. Such ceramic composites are typically sealed with a preceramic polymer

that is converted to a ceramic material upon firing, thereby forming a sealing coating.

A more desirable method for fabricating a fiber-reinforced ceramic composite

30   would be to form the matrix from a liquid that pyrolyzes to a ceramic material.

However, conventional liquid coating techniques require complete infiltration of the

fiber bundles as disclosed, for example, in U.S. Pat. Nos. 5,024,997 (Debaig-Valade et al.) and 5,198,152 (Streckert et al.). According to these patents, complete infiltration of fiber bundles is required in order to obtain optimum mechanical and physical properties. In one such infiltration method, as disclosed in U.S. Pat. No. 5,494,867

5   (Schwab et al.), the fibers are impregnated with a matrix material containing a solvent-free fluid preceramic polymer with up to 70 percent by weight (wt-%) of a ceramic powder. However, such completely infiltrated products can be brittle unless the fibers are first coated with a material that reduces the bonding interaction between the fibers and the matrix material, or porosity is introduced into the matrix material.

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Summary of the Invention

In one aspect, the present invention provides a composite ceramic comprising a ceramic matrix comprising ceramic particles dispersed within a ceramic bonding phase; and a plurality of continuous ceramic fiber bundles (i.e., bundles of continuous ceramic

15   fibers); wherein the ceramic matrix does not completely infiltrate a majority of the individual fiber bundles. In another aspect, the present invention provides articles incorporating the composite ceramic materials.

As used herein, "ceramic" refers to metal- and/or metalloid-containing nonmetallic materials that include crystalline and/or glassy phases. The term does not

20   include amorphous carbonaceous materials.

One embodiment of a ceramic composite material according to the present invention comprises: a ceramic matrix comprising ceramic particles dispersed within a ceramic bonding phase; and a plurality of ceramic fiber bundles, each comprising a plurality of continuous ceramic fibers; wherein the ceramic matrix does not completely

25   infiltrate a majority of the individual fiber bundles, and wherein the ceramic particles have at least one fraction of particles with a median particle size at least as large as the diameter of the largest individual fibers. Preferably, the ceramic particles comprise a coarse fraction having a median particle size at least as large as the diameter of the largest individual fibers and a fine fraction having a median particle size at least 20%

30   less than the median particle size of the coarse fraction. Typically, the coarse particle fraction is present in a greater amount, by weight, than the fine particle fraction.

One embodiment of a ceramic composite material according to the present invention consists essentially of: a ceramic matrix comprising ceramic particles dispersed within a ceramic bonding phase; and a plurality of ceramic fiber bundles, each comprising a plurality of continuous ceramic fibers; wherein the ceramic matrix

5   does not completely infiltrate the individual fiber bundles, and wherein the ceramic particles have at least one fraction of particles with a median particle size at least as large as the diameter of the largest individual fibers.

Yet another embodiment of a ceramic composite material according to the present invention comprises: a ceramic matrix comprising ceramic particles dispersed

10   within a silicon-containing non-oxide ceramic bonding phase; and a plurality of ceramic fiber bundles, each comprising a plurality of continuous ceramic oxide fibers; wherein the ceramic matrix does not completely infiltrate the individual fiber bundles, and wherein the ceramic particles comprise a coarse fraction having a median particle size at least as large as the diameter of the largest individual fibers and a fine fraction having

15   a median particle size at least 20% less than the median particle size of the coarse fraction.

Still another embodiment of a ceramic composite material according to the present invention comprises: a ceramic matrix comprising ceramic particles dispersed within a ceramic bonding phase; and fabric comprising at least one ceramic fiber bundle

20   comprising a plurality of continuous ceramic fibers; wherein the ceramic matrix is in direct contact with less than 70% of the fibers, and wherein the ceramic particles have at least one fraction of particles with a median particle size at least as large as the diameter of the largest individual fibers.

The present invention also provides a U-tube (i.e., a U-shaped tube) comprising

25   ceramic composite material according to the present invention. Such U-shaped tubes are typically used as radiant burner tubes in furnaces. One U-tube according to the present invention comprises: a ceramic matrix comprising ceramic particles dispersed within a ceramic bonding phase; and a plurality of ceramic fiber bundles, each comprising a plurality of continuous ceramic fibers; wherein the ceramic matrix does

30   not completely infiltrate a majority of the individual fiber bundles, and wherein the ceramic particles have at least one fraction of particles with a median particle size at

least as large as the diameter of the largest individual fibers. Preferably, for the U-tube, the ceramic particles comprise a coarse fraction having a median particle size at least as large as the diameter of the largest individual fibers and a fine fraction having a median particle size at least 20% less than the median particle size of the coarse fraction.

5   A method for making ceramic material according to the present invention is also provided. One such method comprises: providing fabric comprising a plurality of ceramic fiber bundles, each bundle comprising a plurality of continuous ceramic fibers; providing a slurry comprising ceramic particles dispersed within a preceramic polymer; wherein the ceramic particles have at least one fraction of particles with a median

10   particle size at least as large as the diameter of the largest individual fibers; coating the slurry on the fabric; and firing the slurry-coated fabric to provide a ceramic matrix that does not completely infiltrate a majority of the individual fiber bundles. Preferably, prior to the step of coating the slurry on the fabric, the method further comprises: forming the fabric into a desired shape; coating the fabric with a carbon-containing

15   resin capable of being pyrolyzed to form a carbonaceous layer; and pyrolyzing the carbon-containing resin to form a shaped fabric. The step of coating the fabric with the carbon-containing resin can be performed prior to the step of forming the fabric.

In certain preferred embodiments, the steps of coating the slurry on the fabric and firing the slurry-coated fabric are repeated at least once. Also, in certain preferred

20   embodiments, the method further includes the steps of coating a second preceramic polymer without ceramic particles dispersed therein on the ceramic composite material; and firing the polymer-coated fabric to provide a ceramic matrix that does not completely infiltrate a majority of the individual fiber bundles.

Another method of making a ceramic composite material comprises: providing

25   fabric comprising at least one ceramic fiber bundle comprising a plurality of continuous ceramic fibers; providing a slurry comprising ceramic particles dispersed within a preceramic polymer; wherein the ceramic particles have at least one fraction of particles with a median particle size at least as large as the diameter of the largest individual fibers; coating the slurry on the fabric; and firing the slurry-coated fabric to provide a

30   ceramic matrix that is in direct contact with less than 70% of the fibers.

Brief Descriptions of the Drawing

FIG. 1 is a schematic representation of a cross-section of a portion of a composite material according to the present invention; and

FIG. 2 is a perspective view of a U-shaped tube utilizing composite material according to the present invention.

Detailed Description

Referring to FIG. 1, composite material according to the present invention 10 includes fabric of continuous ceramic fiber bundles 12 comprising individual fibers 13, ceramic particles 14, and ceramic bonding phase 16. The representation shown in FIG. 1 is a portion of the composite material according to the present invention showing two orthogonally oriented fiber bundles. The ceramic matrix (i.e., the ceramic bonding phase 16 and ceramic particles 14) does not completely infiltrate a majority of the individual fiber bundles. Preferably, the ceramic matrix (i.e., the ceramic bonding phase 16 and ceramic particles 14) does not completely infiltrate any of the individual fiber bundles. The bundles of fibers can be in the form of rovings, tows, yarns, or other groups of fibers. The fabric can be woven, braided, or knitted continuous fiber bundles, although other configurations (e.g., filament wound) of continuous fiber bundles are also useful. The term "continuous fiber" is intended to refer to a fiber having a length that is relatively infinite when compared to the fiber diameter. In practical terms, such fibers have a length on the order of about 15 centimeters (cm) to at least several meters, and may even have lengths on the order of kilometers or more.

Significantly, in ceramic composite material according to the present invention, the ceramic matrix does not completely infiltrate a majority of the individual fiber bundles. That is, although the ceramic matrix may completely infiltrate some of the bundles, a majority of them do not have ceramic matrix within the fiber bundles such that ceramic matrix is completely surrounding each and every individual fiber within the bundles. In this way, a majority of the outer fibers of the fiber bundles are bound to the ceramic matrix, whereas a majority of the internal fibers of the fiber bundles are not. As a result, there is strong bonding between the matrix and individual fiber bundles, but not between the matrix and all individual fibers. Although not wanting to be bound by

theory, this configuration allows fibers to deform elastically (as by stretching) and/or mechanically (as by untwisting) and thereby reduce crack formation and propagation in the composite. Significantly, this can occur without sacrificing the density and strength of the matrix. Thus, because the matrix bonds to only some of the fibers of the bundles in the composite materials according to the present invention, the remaining fibers are free to move independently of the matrix and span cracks that may be present. Although there may be a certain level of bonding between the matrix and some internal fibers of a bundle, it is believed that overall the fibers will function effectively to support a load across the crack. Therefore, the present invention allows relatively strong, tough ceramic composites to be made without special fiber coatings (although they can be used if desired) or weak porous matrices.

Typically, and preferably, the greater the percentage of fibers in the fiber bundles that are not tightly bonded to the matrix, the more effective the fibers are at reducing crack formation and catastrophic failure of the composite. Thus, the larger the fiber bundle, the greater the percentage of fibers that are not in direct contact with, and bonded to, the ceramic matrix. Preferably, less than 70% (more preferably, less than 50%) of the individual fibers are in direct contact with, and bonded to, the ceramic matrix. As a result, composite materials according to the present invention that have larger bundles typically have higher fracture toughness than composite materials with smaller bundles (i.e., bundles with fewer numbers of fibers). Depending on the method of producing a composite ceramic material, however, the fracture toughness can vary even though the size of the bundles is the same.

Ceramic matrices utilized in the present invention include ceramic particles dispersed within a ceramic bonding phase. These ceramic matrices partially infiltrate the fiber bundles, thereby producing a relatively inexpensive ceramic composite that is relatively tough and has a relatively dense matrix such that the overall composite is substantially impermeable to air at room temperature (i.e., 20-25°C). Such matrices can be formed, for example, by firing a slurry containing a polymeric ceramic precursor material (i.e., preceramic polymer) and ceramic particles, at least a fraction of which have a median particle size that is at least as large as the largest diameter of the fibers.

By forming the matrix from a slurry containing a polymeric ceramic precursor material and ceramic particles, it is possible to form a composite ceramic material that is both relatively tough and substantially impermeable (e.g., impermeable to air at room temperature). Although not intending to be bound by theory, it is believed that this results from a selection of ceramic particles having a median particle size (i.e., the longest dimension of the particles) that is at least as large as the diameter of the largest individual fibers in a bundle. The particles are believed to reduce the infiltration of the polymeric ceramic precursor material into the fiber bundles. As a result, the matrix is generally confined to the outer fibers of a majority of the fiber bundles, thereby resulting in ceramic fibers that are not fused together or fused to the matrix material.

Because matrix material does not completely infiltrate the fabric (i.e., fill every void within and between the fiber bundles), composite materials according to the present invention are believed to have internal pores (e.g., voids between fiber bundles), although overall, the composite materials are not permeable. This is believed to result from the matrix material blocking off or sealing the pores. This can be demonstrated, for example, by microscopic evaluation of a cross-section of the fabric, which typically shows matrix spanning the space between the bundles. Referring again to FIG. 1, ceramic particles 14 form a deposit (as in a filter cake) on the outer surface of the fiber bundles 12, thereby limiting penetration of ceramic bonding phase 16 into the fiber bundles 12.

In contrast, forming the matrix from the chemical vapor deposition of silicon carbide and/or silicon nitride does not typically produce a composite material that is both tough and impermeable (e.g., to air at room temperature) without subsequent sealing coatings. Rather, composite materials that are either, but not both, tough or impermeable to air at room temperature, can be produced using chemical vapor deposition techniques. Although not wanting to be bound by theory, it is believed that this occurs because the matrix grows radially from the surface of the fiber bundle when the matrix is formed using chemical vapor deposition. Also, in textiles and engineered yarns (e.g., yarns that are twisted and/or plied together or texturized), the voids between fiber bundles are typically scaled to the size of the bundles. Thus, the bigger the fiber

bundles, the bigger the voids, and the more permeable is the composite ceramic material.

As a result of the presence of nonfused fibers (either to themselves or to the ceramic matrix), composite materials according to the present invention typically

5   exhibit "composite" fracture properties rather than "monolithic" fracture properties, such as is described in U.S. Pat. No. 5,476,684 (Smith). Thus, fracture properties of composite materials according to the present invention are characterized by producing, on fracturing, a fracture surface that is populated with the fracture ends of numerous ceramic fibers in a brush-like array. That is, ceramic composites according to the

10   present invention have fibers sticking out from a fracture surface, exhibiting what is generally referred to as "fiber pullout." A fracture surface having such fiber pullout is described as being "brushy." A brushy fracture surface is characteristic of a composite article having ceramic fibers that have not significantly fused together or to the matrix material.

15   Composite materials according to the present invention are substantially impermeable to air at room temperature. Preferably, composite materials according to the present invention have a permeability of less than about 20 x

10^{-4} liters per hour square centimeter ($l/h \cdot cm^2$), and more preferably, less than about 10 x 10^{-4} $l/h \cdot cm^2$, measured according to the procedure described in the Examples. Lower

20   permeabilities can be obtained through the use of a sealing coating as described below.

Composite materials according to the present invention are relatively tough such that cracks are inhibited from enlarging or extending. Preferably, they have a fracture toughness of at least about 3 MPam$^{1/2}$, and more preferably, a toughness of at least about 5 MPam$^{1/2}$. Typically, composite materials according to the present invention

25   have a toughness of no greater than about 15 MPam$^{1/2}$, measured according to the procedure described in the Examples.

Composite materials according to the present invention typically have a dense matrix material. By this it is meant that the matrix material (as opposed to the overall composite) is not significantly porous, and provides an article that will retain its shape

30   under conditions of use. Preferably, the density of the composite material (as opposed to the matrix material) is at least about 1.7 grams per cubic centimeter (g/cm^3) and no

greater than about 2.5 g/cm^3. More preferably, the density is about 1.9 g/cm^3 to about 2.2 g/cm^3, and most preferably, about 2.0 g/cm^3 to about 2.1 g/cm^3.

Typically, and preferably, the ceramic fiber bundles, the ceramic bonding phase, and the ceramic particles are selected and arranged taking into account differences in the thermal expansion coefficients of the components. Further, the ceramic fiber bundles should be compatible with the ceramic bonding phase. That is, the bonding phase should not substantially degrade the strength of the fibers during processing and/or heat treatment. Thus, preferably, the bonding phase is substantially free of components that would promote fiber degradation. For example, for ceramic oxide fibers, components containing elements such as Cr, Ni, Na, and Co should be avoided or minimized, whereas for ceramic carbide fibers, components containing elements such as Fe should be avoided or minimized.

Suitable ceramic fibers are those that are resistant to the temperatures required to transform the particular polymeric ceramic precursor material utilized into ceramic material. Suitable ceramic fibers include ceramic oxide fibers such as alumina fibers, aluminosilicate fibers, aluminoborosilicate fibers, zirconia fibers, yttria-alumina fibers, as well as silicon carbide fibers, silicon nitride fibers, or combinations thereof. Preferred fibers are ceramic oxide fibers. Preferred ceramic oxide fibers include aluminosilicate fibers, aluminoborosilicate fibers, and alumina fibers. Typically, and preferably, the ceramic fibers in the composite material are crystalline ceramics and/or a mixture of crystalline ceramic and glass (i.e., fibers containing both crystalline ceramic and glass phases). This term is also used herein to include high temperature glass fibers, such as leached glass fibers, which are available, for example, under the trade designation "REFRASIL" from Armco Inc., Middletown, OH.

Preferably, the ceramic fibers have a diameter in a range of about 3 micrometers to about 100 micrometers. Fibers having diameters substantially greater than about 100 micrometers are typically not as strong as fibers in the preferred range and tend to be difficult to weave, braid, or otherwise form into a desired shape. More preferably, the fibers have a diameter in a range of about 3 micrometers to about 50 micrometers. Even more preferably, the fibers have a diameter in a range of about 5 micrometers to about 15 micrometers. Most preferably, the fibers have a diameter in a range of about 7

micrometers to about 13 micrometers. The fibers in fabric used to make composite materials according to the present invention can be of differing diameters.

Preferably, fibers used to make composite materials according to the present invention have an average tensile strength of greater than about 700 megapascals

5   (MPa). More preferably, the average tensile strength of the fibers is greater than about 1200 MPa; even more preferably, greater than about 1800 MPa; and, most preferably, greater than about 2100 MPa.

Methods for making suitable alumina fibers are known in the art and include that disclosed in U.S. Pat. No. 4,954,462 (Wood et al.). Preferably, the alumina fibers

10   comprise, on a theoretical oxide basis, greater than about 99 percent by weight Al_2O_3 and about 0.2-0.5 percent by weight SiO_2, based on the total weight of the alumina fibers. Preferred alumina fibers are commercially available, for example, under the trade designation "NEXTEL 610" from the 3M Company of St. Paul, MN.

Methods for making suitable zirconia fibers are known in the art and include

15   that disclosed in Reissued U.S. Pat. No. 35,143 (Funkenbusch et al.). Yttria-alumina fibers can be made, for example, as disclosed in U.S. Pat. No. 5,348,918 (Budd et al.).

Suitable aluminosilicate fibers are described, for example, in U.S. Pat. No. 4,047,965 (Karst et al.). Preferably, the aluminosilicate fibers comprise, on a theoretical oxide basis, about 67 percent to about 85 percent by weight Al_2O_3 and

20   about 33 percent to about 15 percent by weight SiO_2, based on the total weight of the aluminosilicate fibers. Some preferred aluminosilicate fibers comprise, on a theoretical oxide basis, about 67 percent to about 77 percent by weight Al_2O_3 and about 33 percent to about 23 percent by weight SiO_2, based on the total weight of the aluminosilicate fibers. One preferred aluminosilicate fiber comprises, on a theoretical

25   oxide basis, about 85 percent by weight Al_2O_3 and about 15 percent by weight SiO_2, based on the total weight of the aluminosilicate fibers. Another preferred aluminosilicate fiber comprises, on a theoretical oxide basis, about 73 percent by weight Al_2O_3 and about 27 percent by weight SiO_2, based on the total weight of the aluminosilicate fibers. Preferred aluminosilicate fibers are commercially available, for

30   example, under the trade designations "NEXTEL 550" and "NEXTEL 720" from the 3M Company of St. Paul, MN.

Suitable aluminoborosilicate fibers are described, for example, in U.S. Pat. No.
3,795,524 (Sowman). Preferably, the aluminoborosilicate fibers comprise, on a
theoretical basis, about 55 percent to about 75 percent by weight Al_2O_3, less than about
45 percent (preferably, less than about 44 percent) by weight SiO_2, and less than about
5   25 percent (preferably, about 1 percent to about 5 percent) by weight B_2O_3,
respectively, based on the total weight of the aluminoborosilicate fibers. Preferred
aluminoborosilicate fibers are commercially available, for example, under the trade
designations "NEXTEL 312" and "NEXTEL 440" from the 3M Company.

Ceramic fibers are typically available grouped together in the form of yarns or
10   tows (i.e., one or more rovings, which are a plurality of continuous, parallel fibers
without twist), for example. Such yarns or tows typically include about 400 to about
7800 individual ceramic oxide fibers and generally have a diameter of about 0.2
millimeter (mm) to about 1.5 mm. Yarn diameters in this range typically have superior
textile qualities as compared to yarns with diameters outside of this range. Ceramic
15   yarn can be ply-twisted, which means that two or more yarns are twisted together. This
typically is done to increase the strength of the yarn. It should be understood, however,
that fiber bundles do not necessarily have to be twisted.

The continuous ceramic fibers can be in the form of woven, braided, or knitted
fabrics, although other configurations (e.g., filament wound fibers) are also useful. The
20   ceramic fibers can be provided in fabric and filament wound forms by techniques
known in the art (see, e.g., U.S. Pat. Nos. 5,180,409 (Fischer et al.) and 5,453,116
(Fischer et al.)). Woven fabrics are also commercially available, for example, under the
trade designation "NEXTEL WOVEN FABRICS" from the 3M Company. Weaves for
the woven fabrics include single plain weaves and multi-axial weaves. Braids for the
25   braided fabric include plain, open, and triaxial braids.

As-received fibers and fabrics comprising the fibers typically include an organic
sizing material added to the fiber during their manufacture to provide lubricity and to
protect the fiber strands during handling. Conventional sizing materials include
dextrinized starch gum, gelatin, polyvinyl alcohol, hydrogenated vegetable oils, and
30   nonionic detergents. It is believed that the sizing tends to reduce the breakage of fibers,
reduce static electricity, and reduce the amount of dust during, for example, conversion

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to a fabric. The sizing can be removed, for example, by dissolving or burning it away, although this is not necessary.

In methods according to the present invention, the fabrics are preferably initially coated with a carbon-containing resin (i.e., a solution or dispersion of monomers, oligomers, polymers, or mixtures thereof) for shape retention while the slurry containing the polymeric ceramic precursor material and ceramic particles is applied. Alternatively, fiber coatings such as metal carbides, borides, oxides, and nitrides can be used for shape retention while the slurry containing the polymeric ceramic precursor material and ceramic particles is applied. Of these fiber coatings, preferably, a carbon-containing resin is used.

The carbon-containing resin often washes the sizing off, although typically it is believed that the sizing combines with the carbon-containing resin and is pyrolyzed along with the carbon-containing resin upon subsequent heating. Suitable carbon-containing resins for shape retention are those that are capable of bonding the fiber bundles together to form a stable shape upon pyrolysis of the carbon-containing resin. Preferably, they form a carbonaceous residue with a high carbon content upon pyrolysis. Thus, the composite materials of the present invention typically have a thin carbonaceous coating on the fibers. As used herein, "carbonaceous" means that substantially all the carbon present is amorphous.

Examples of such carbon-containing resins (preferably, organic-based resins) include phenolic resins (available, for example, under the trade designations "BKUA 2370" from Georgia Pacific, Corp., Atlanta, GA, and "DURIRTE SC-1008" from Borden Chemical, Morganton, NC, which may include particulate material such as boron nitride particles (as disclosed in EP Publication 0 528 411)); corn syrup containing aluminum monohydrate and ammonium chloride; an aqueous solution of sucrose; and an aqueous solution of corn syrup solids. Of these resins, the phenolic resins are preferred because of their high carbon content upon pyrolysis. Phenolic resins include a wide variety of products that result from the reaction product of phenols and aldehydes. Phenolic resins include, for example, acid catalyzed phenolic resins and base catalyzed phenolic resins. Of the phenolic resins, those that can be diluted with water are the most preferred.

Typically, composite materials according to the present invention include only about 4 weight percent to about 6 weight percent carbonaceous material, based on the total weight of the fiber having the carbonaceous material thereon (without the ceramic matrix). This is believed to be significantly lower than the amount of carbonaceous

5   material needed in conventional composite materials to reduce bonding between the matrix material and the fibers.

The ceramic bonding phase is preferably a non-oxide. More preferably, it is a silicon-containing non-oxide, such as silicon carbide or silicon nitride, and other ceramic materials that do not contain oxygen (although it is noted that silicon carbide

10   typically has a thin layer of SiO_2 on its exposed surfaces). Such materials are preferred over ceramic oxide bonding phases because oxides do not typically form dense matrices. For example, if a silicon-containing ceramic precursor were fired in oxygen and converted to a ceramic bonding phase, the silicon would oxidize and expand to form a porous, fractured solid. These bonding phases are typically formed from a

15   silicon-containing ceramic precursor polymer, which is exposed to an inert atmosphere (i.e., a nonreactive atmosphere such as nitrogen) at an elevated temperature.

Typically, a polymeric ceramic material is chosen such that the resultant ceramic bonding phase is compatible with the ceramic particles and ceramic fibers. That is, the bonding phase preferably does not substantially degrade or react with the

20   ceramic particles or ceramic fibers during processing and/or heat treatment. Furthermore, the bonding phase is substantially free of components which would promote degradation of the ceramic oxide particles or ceramic oxide fibers. Examples of suitable silicon-containing precursors for the ceramic bonding phase include polyureasilazanes (available, for example, under the trade designation "CERASET SN"

25   from Commodore Polymer Technologies, Inc., Columbus, OH (and was formerly available under such trade designation from Lanxide Corp., Newark, DE)), polycarbosilanes (available, for example, under the trade designation "NICOLON" from Dow Corning, Midland, MI), polyhydridosiloxanes (available, for example, under the trade designation "SILICON RESIN MK" from Wacker Chemical Corp., Adrain,

30   MI), and vinylic polysilanes available from Union Carbide, Danbury, CT.

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If desired, the materials used to make the bonding phase of the particle-containing matrix material can also be used without particles in an overcoating, which is referred to herein as a sealing coating. This is typically done to further reduce the permeability of the composite material to air at room temperature and/or to strengthen

5   the ceramic matrix. Such sealing coatings are used in conventional CVD coated ceramic composites.

Suitable ceramic particles include ceramic oxide (e.g., alumina, zirconia, yttria, mullite, hafnia, and silica), carbide (e.g., SiC), and nitride (e.g., Si_3N_4) particles, and combinations thereof. Typically, the ceramic particles have particle sizes (as measured

10   from the largest dimension of the particle) ranging from about 0.1 micrometer to about 20 micrometers (preferably, about 0.1 micrometer to about 10 micrometers and more preferably, about 0.2 micrometer to about 1 micrometer). Preferably, the median particle size of at least one fraction of the particles are matched to the diameter of the fibers for formation of a tough composite material. More preferably, the particles

15   include two or more fractions of material having different median particle sizes. For example, a bimodal distribution of particles can be used which includes a coarse particle fraction having a median particle size at least as large as the largest diameter of the fibers and a fine particle fraction having a median particle size that is about 20% less (and frequently, about 10 times less) than that of the coarse particles. The coarse

20   fraction is typically used in a greater amount (e.g., at least about 3 times greater by weight) than the fine fraction.

Suitable ceramic oxide particles can be made by techniques known in the art, including conventional sol-gel techniques. Particles can also be made, for example, by crushing or otherwise breaking ceramic oxide bodies into the desired particle sizes, and

25   screening to provide the desired sized particles and distribution. Suitable ceramic oxide particles or bodies can be made by techniques such as those disclosed in U.S. Pat. Nos. 3,795,524 (Sowman), 4,047,965 (Karst et al.), 4,314,827 (Leitheiser et al.), 4,770,671 (Monroe et al.), 4,744,802 (Schwabel), 4,881,951 (Wood et al.), 4,954,462 (Wood), 4,964,883 (Morris et al.), 5,164,348 (Wood), 5,348,918 (Budd et al.), (Larmie),

30   5,139,978 (Wood), 5,219,806 (Wood), 5,429,647 (Larmie), 5,489,204 (Conwell et al.), 5,489,318 (Erickson et al.), 5,498,269 (Larmie), and 5,516,348 (Conwell et al.),

Reissued U.S. Pat. No. 35,143 (Funkenbusch et al.), and PCT Application No.
PCT/US93/12441 having International Publication No. WO 94/14722, published July
7, 1994. Further, alumina particles are available, for example, under the trade
designations "HPA 0.05" from Ceralox, Tuscon, AZ. Zirconia particles are available,
for example, under the trade designations "ATZ80" from Zirconia Sales Inc., Marietta,
GA. Yttria particles, are available, for example, from Ceralox. Mullite particles are
available, for example, under the trade designations "MULCR" from Baikowski,
Charlotte, NC. Hafnia particles are available, for example, from Johnson-Mathey,
Ward Hill, MA. Silica particles are available, for example, under the trade designation
"IMSIL A-8" from Unimin Corp., Elco, IL.

The coating compositions can be made, for example, by preparing a mixture
(i.e., slurry) of ceramic oxide particles and a polymeric ceramic precursor material.
Optionally, the slurry can include, if desired, an organic solvent, as well as additives
such as free-radical initiators (e.g., peroxides such as dicumyl peroxide as well as 2,5-
bis-(tert-butylperoxy)-2,5-dimethyl-3-hexyne, 1,1-bis(tert-butylperoxy)-3,3,5-
trimethylcyclohexane, and 2,5-dimethyl-2,5-di-(2-ethyl-hexanoylperoxy)hexane), and
crosslinkers (e.g., vinyl crosslinkers). Organic solvents that may be useful include
alcohols (e.g., ethanol and isopropanol), ketones (e.g., acetone and methylethyl ketone),
hydrocarbons (e.g., mineral spirits), and mixtures thereof. The viscosity of the coating
composition can be adjusted, for example, by the amount of organic solvent used, or by
other techniques which should be apparent to one skilled in the art, including the
addition of thickening agents, thinning agents, wetting agents, etc.

Preferred slurries include polymeric ceramic precursor material and ceramic
particles. More preferred slurries include polymeric ceramic precursor material,
ceramic particles, and a free-radical initiator. Polymeric ceramic precursor material is
preferably present in an amount of about 15 percent by weight to about 30 percent by
weight, based on the total weight of the slurry. Coarse ceramic particles are preferably
present in an amount of about 50 percent by weight to about 70 percent by weight,
based on the total weight of the slurry. Fine ceramic particles are preferably present in
an amount of about 10 percent by weight to about 30 percent by weight, based on the
total weight of the slurry. A free-radical initiator is used typically in an amount of up to

about 0.2 percent by weight, based on the total weight of the slurry. Most preferred slurries also include an organic solvent and a wetting agent. An organic solvent is used typically in an amount of about 10-30 percent by weight, based on the total weight of the slurry. A wetting agent is used typically in an amount of about 0.1-0.5 percent by weight, based on the total weight of the slurry.

One method for making composite materials according to the present invention includes coating (e.g., via brush coating, pour coating, dip coating, roll coating, or spray coating) ceramic oxide fiber fabric with a coating composition (e.g., slurry containing polymeric ceramic precursor material and ceramic particles), and then shaping the fabric as desired. For example, the fabric can be fitted over a mandrel that is in the desired shape. Alternatively, for example, ceramic oxide fiber can be filament wound (e.g., helically winding or cross-winding) over a mandrel and the wound fiber saturated with a coating composition. Another exemplary approach is to coat ceramic oxide fiber fabric with a carbon-containing resin for shape retention, shape the fabric as desired, and then pyrolyze the carbon-containing resin to a char (preferably, in an inert atmosphere at a temperature of about 500-700°C) to provide the fabric in the desired shape. The resulting shaped fabric can then be coated with slurry containing polymeric ceramic precursor material and ceramic particles.

The coating compositions of the resulting filter material preform are typically dried and conventionally cured prior to firing. Firing times and temperatures are dependent, for example, on the particular polymeric material(s) used. Typical firing temperatures range from about 700°C to about 1050°C. Typically, the polymeric material is fired at a temperature substantially below the degradation temperature of the fibers, thereby forming a ceramic matrix at the same time as it is being bonded to the reinforcing fibers. If the firing temperatures are low enough, the composite can be formed from fibers that are less expensive. Firing times, depend, for example, on the configurations of the composite material and the particular polymeric materials used.

The coating compositions (i.e., slurries containing polymeric ceramic precursor material and ceramic particles) can be coated on the preform in one or more applications as desired, with drying and/or firing between applications. For example, one layer or application of the composition can be applied and fired followed by

17

another layer or application of the composition. Additionally, the polymeric ceramic

precursor material, either the same or different than that used in the slurry with the

ceramic particles, can be applied in an overcoating (i.e., a sealing coating) to further

seal the composite material. This material can be applied, dried, and fired as described

5   above for the slurry.

Typically, composite materials according to the present invention are capable of

being used in applications (e.g., furnace and other high temperature applications) at

temperatures in a range of about 300°C to about 1200°C (more typically, about 500°C to

about 1000°C).

10   Articles, such as tubular articles, truncated cones, flat plates, and corrugated

plates, employing composite material according to the present invention can be

fabricated to the size needed for the desired application. An example of a tubular

article (e.g., a U-tube) is described in U.S. Pat. No. 5,350,139 (Leyderman). Referring

to FIG. 2, tubular article 20 has first straight portion 22, second straight portion 24, and

15   arcuate portion 26. Arcuate portion 26 is located between first and second straight

portions 22 and 24, and is integral therewith. That is, the tubular article is made from

one piece, rather than being made from three separate parts that are subsequently pieced

together. As used herein, "arcuate" means having a bend, not necessarily a bend with a

constant radius.

20   Objects and advantages of this invention are further illustrated by the following

examples, but the particular materials and amounts thereof recited in these examples, as

well as other conditions and details, should not be construed to unduly limit this

invention. All parts and percentages are by weight unless otherwise indicated.

25   **Examples**

Matrix Precursor Slurry Preparation

A mixture of 100 grams of silicon carbide particles (available under the trade

designation "C1200 SILICON CARBIDE" from Fujami Corp., Elmhurst, IL), 30 grams

of silicon carbide particles (available under the trade designation "UF-15 SILICON

30   CARBIDE" from H.C. Starck, Inc., Newton, MA) having particle sizes of about 10

micrometers and 1 micrometer, respectively, 40 grams of polyureasilazane resin

(obtained under the trade designation "CERASET SN" from Lanxide Corp., Newark, DE), 1.3 gram of dicumyl peroxide (available from Aldrich Chemical Co., Milwaukee, WI), 1.3 grams of an alkyl organic phosphate ester acid wetting agent (available under the trade designation "EMPHOS PS-21A" from Witco Materials Corp., Chicago, IL),

5   and 40 grams of odorless mineral spirits was placed in a 1.1 liter (0.3 gallon) ceramic jar containing 1000 grams of 2.5 centimeter diameter ceramic alumina balls and the mixture milled at 60 revolutions per minute (rpm) for approximately 12 hours to produce a uniform slurry.

10   **Example 1**

A flat panel composite material was formed from braid panel (approximately 9 cm x 12 cm) prepared by flattening a portion of a ceramic fiber braid (aluminoborosilicate fibers) having a construction consisting of four ends per carrier of 900 denier 1/2 yarns at 10 picks per inch, braid angle +/- 53° (which typically have

15   about 390 fibers per bundle, available under the trade designation "NEXTEL 312 2-INCH BRAIDED SLEEVING" from the 3M Company, St. Paul, MN). A phenolic resin emulsion, prepared by diluting 1 part phenolic resin (available under the trade designation "BKUA-2370" from Georgia Pacific, Corp., Atlanta, GA) with 5 parts distilled water, was sprayed onto the panel and cured at 200°C in air for 15 minutes to

20   produce a stabilized panel. The stabilized panel was then heated to 1000°C at a heating rate of 100°C per hour in a nitrogen atmosphere, and then held at 1000°C for approximately 30 minutes to pyrolyze the phenolic resin, producing a thin carbon coating on the ceramic fibers. The resin add-on was 6 wt-%. That is, there was 6 wt-% carbonaceous material on the fiber, based on the total weight of the fiber and

25   carbonaceous material.

The above-described matrix precursor slurry was applied to the pyrolyzed panel by dipping the panel into the slurry, allowing excess slurry to drip from the panel, air drying the panel at room temperature to a constant weight (such that all the mineral spirits are evaporated), dipping the panel into the slurry a second time, allowing excess

30   slurry to drip from the panel, and then air drying the coated article at room temperature to a constant weight. The dried, slurry coated panel was then fired in a nitrogen

atmosphere, according to the following schedule: room temperature to 1000°C at 100°C/hour; and held at 1000°C for one hour. The panel was then cooled to room temperature at a rate of 5°C/minute to 10°C/minute.

A second matrix coating was applied to the pyrolyzed composite panel by
5 following the same procedure (i.e., dipping in the slurry, drying, dipping a second time, drying, and firing at 1000°C) to produce a composite that contained approximately 61 wt-% silicon carbide (SiC) matrix, as determined by weight differential between the fired composite and the pyrolyzed panel.

A cross-section of the composite panel was prepared by cutting the panel
10 perpendicular to the course of the yarns in the braid, mounting the cross-sectioned sample in a 2.54 cm cold mounting ring form with the yarns perpendicular to the surface of the mounting that would be polished, filling the mold with an epoxy resin (available under the trade designation "EPO-MIX" from Buehler Ltd., Lake Bluff, IL) under a vacuum at room temperature, and allowing the resin to cure overnight at room
15 temperature. The cured sample was then polished using polishing equipment obtained from Buehler, Ltd. (i.e., products available under the trade designations "AUTOMET 2 POWERHEAD" and "ECOMET GRINDER") using a sequence of 70, 45, 30, 15, 9, 6, 3, and 1 micrometer diamond grinding/polishing discs to produce a mirror-like finish on the mounting which showed, at 500x magnification, no visible indication of
20 chipping on the fiber edges.

Fiber bundle cross-sectional area was determined by selecting an average of at least 8 bundles containing 50 or more fibers, measuring the cross-sectional area of those bundles including fibers which were in contact with the matrix material, and calculating the average number of fibers per unit area. The number of fibers free of the matrix
25 material was then estimated based on visual inspection of the fiber bundles at 500x magnification. Free fiber estimates based on this analytical sequence are ±10% at a 95% confidence level.

The fiber bundles in the cured composite had an average cross-section of 2.0 millimeters (mm) x 0.4 mm. Microscopic examination of a cross-section of the test
30 coupon indicated that approximately 20% of the fibers in the fiber bundles were in direct contact with matrix material. This included the majority of the outer fibers in

each bundle, although there were some islands of matrix within some of the bundles contacting some internal fibers.

The fracture toughness of the composite, which was determined as described in ASTM E399-81 test procedure, published 1981, for plane strain fracture toughness testing, increased with increased crack length, reaching a maximum value of 4 MPam$^{1/2}$. Microscopic examination of the fracture surfaces of the test coupon showed evidence of fiber "pull out" or a "brushy failure" as described in U.S. Pat. No. 5,476,684 (Smith).

Example 2

A flat panel composite was formed substantially as described in Example 1 except that a flattened braid panel having 10 ends per carrier of 1800 denier 1/2 at 6 picks per inch, braiding angle +/- 62° (which typically have about 720 fibers per bundle, available under the trade designation "NEXTEL 312 4-INCH BRAIDED SLEEVING" from the 3M Company) was used. The fiber bundles in the cured composite had an average cross-sections of 4.0 mm x 0.8 mm. The composite contained approximately 61 wt-% SiC matrix. Microscopic examination of a cross-section of the test coupon, at 500x magnification, indicated that approximately 10% of the fibers in the fiber bundles were in direct contact with matrix material. This included the majority of the outer fibers in each bundle, although there were some islands of matrix within some of the bundles contacting some internal fibers.

The density of the flat panel was determined by measuring the external dimensions of the flat panel for the volume and dividing that into the weight of the flat panel. The density measured in this manner was 2.1 grams/centimeter^3 (g/cm^3).

The fracture toughness of the composite increased with increased crack length, reaching a maximum value of 12 MPam$^{1/2}$. Microscopic examination of the fracture surfaces of the test coupon showed evidence of fiber "pull out" or a "brushy failure."

Example 3

A flat panel composite was formed substantially as described in Example 1 except that the flattened braid panel was replaced by a 20 cm x 20 cm piece of ceramic

fabric which had two 900 denier yarns twisted together and woven in a plain weave
(available under the trade designation "AF-14" from the 3M Company). The fiber
bundles in the cured composite had an average cross-section of 0.8 mm x 0.2 mm. The
composite contained approximately 65 wt-% SiC matrix. A test coupon of the

5   composite was manually fractured and the fracture surfaces subjected to microscopic
examination. The fracture was a "brushy failure" typical of the tough fracture exhibited
by the composites of Examples 1 and 2 with an estimated 40% of the fibers exhibiting
"pull out."

10   **Example 4**

A flat panel composite was prepared substantially as described in Example 3
except that a ceramic fabric having two yarns of 1800 denier fiber twisted together and
woven in a 5 harness satin (available under the trade designation "AF-40" from the 3M
Company) was used in place of the plain weave ceramic fabric. The fiber bundles in the

15   cured composite had an average cross-section of 1.1 mm x 0.3 mm. The composite
contained approximately 63 wt-% SiC matrix. Microscopic examination of a cross-
section of the composite, at 500x magnification, showed that approximately 30% of the
fibers within the bundles were in direct contact with the matrix material. This included
the majority of the outer fibers in each bundle, although there were some islands of

20   matrix within some of the bundles contacting some internal fibers.

The density of the flat panel was determined by the procedure outlined in
Example 2. The density measured in this manner was 1.9 g/cm³.

A test coupon of the composite was manually fractured and the fracture surfaces
subjected to microscopic examination. The fracture was a "brushy failure" typical of

25   the tough fracture exhibited by the composites of Examples 1-3 with an estimated 60%
of the fibers exhibiting "pull out."

Example 5

A flat panel composite was formed substantially as described in Example 1

30   except that the flattened braid panel was replaced with two layers (0.19 g/cm² total
weight) of a braid having 10 ends per carrier of 900 denier 1/2 at 4.1 picks per inch,

braiding angle +/- 56° (available under the trade designation "NEXTEL 312 4-INCH BRAIDED SLEEVING" from the 3M Company).

The density of the flat panel was determined by the procedure outlined in Example 2. The density measured in this manner was 12.0 g/cm^3.

5   The permeability of the composite was determined using Test Procedure ASTM D-737-96 by clamping the composite in a test fixture, pressurizing one side of the composite to 124 Pascals and observing the pressure drop through a 38.7 cm^2 (6 inch^2) area of the composite. Permeability data for the composite, which contained 63 wt-% SiC matrix, is reported in Table 1, below.

10

Example 6

A flat panel composite was prepared substantially as described in Example 2 except braid weight was 0.20 g/cm^2 and the composite contained 58 wt-% SiC matrix. Permeability data for the composite, which was determined as described in Example 5,

15   is reported in Table 1, below.

Comparative Example C-1

A nonwoven mat (50 g/m^2 basis weight) was formed from aluminoborosilicate fibers (available under the trade designation "NEXTEL 312" from the 3M Company).

20   Tows of 10-12 micrometer diameter fibers were chopped into 2.5 cm staple length using a conventional glass roving cutter. The chopped fibers were formed into a nonwoven fabric using conventional web forming equipment and procedures (as described in U.S. Pat. No. 5,380,580 (Rogers et. al.)). The web was stabilized with phenolic resin ("BKUA-2370") substantially as described in Example 1 except that the

25   pyrolysis was carried out with the following schedule: room temperature to 600°C in a nitrogen atmosphere at 100°C/hour; 600°C to 1000°C in a hydrogen atmosphere at 100°C/hour; and held At 1000°C in a hydrogen atmosphere for one hour. The material was cooled to room temperature at a rate of 5-10 °C /minute.

The resin add-on was 10 wt-%. That is, there was 10 wt-% carbonaceous material on

30   the fiber, based on the total weight of the fiber and carbonaceous material.

A silicon carbide matrix was deposited on the pyrolyzed web through the decomposition of methyl trichlorosilane at 1000 °C in a vacuum chemical vapor deposition reactor, as described in Example 1 of U.S. Pat. No. 4,397,901 (Warren), to produce a brittle composite article having 70 wt-% SiC matrix. The composite article was readily broken by manual flexing and visual examination of the fracture surface showed no signs of fiber "pull out" (i.e., a "non-brushy failure"). Microscopic examination of the fracture surface showed the SiC matrix was in direct contact with virtually every fiber.

This example demonstrates that a composite structure having substantially complete infiltration of the matrix material such that it contacts virtually every fiber exhibits brittle failure. In contrast, composite articles according to the present invention which have only partial matrix infiltration are tougher materials which exhibit fiber "pull out" or "brushy failure."

Comparative Example C-2

A braided sleeve of 900 denier 1/2 2.7Z braid of fibers, 6 ends per braid, 6.5 picks per 2.54 cm, 7.62 cm in diameter (available under the designation "NEXTEL 312 3-INCH BRAIDED SLEEVING" from the 3M Company), was flattened, coated with phenolic resin ("BKUA-2370"), pyrolyzed and then coated with silicon carbide as described in Comparative Example C-1 to produce a composite article having 63 wt-% SiC matrix. The fracture toughness increased with increased crack length, reaching a maximum value of over 20 MPam$^{1/2}$. Microscopic examination at 5x-20x of the fracture surfaces of test coupons showed considerable fiber "pull out" or "brushy failure."

This example demonstrates that composite articles which exhibit a tough, "brushy failure" can be prepared by chemical vapor deposition of the SiC matrix material on a reinforcing fabric or braid if the SiC matrix does not completely infiltrate the fiber bundle.

Comparative Example C-3

A flat panel composite was prepared substantially as described in Comparative

Example C-2 except that the 900 denier braid was replaced with a single layer of a

flattened braid of 1800 denier 1/2, 6 picks per inch, braiding angle +/- 62° (0.20 g/cm^2)

(available under the designation "NEXTEL 312 6-INCH BRAIDED SLEEVING" from

5   the 3M Company). Permeability data for the flat panel composite, which contained 63

wt-% SiC matrix, was determined using the method described in Example 5. The

results are reported in Table 1, below.

The flat panel was tough and resistant to fracture as evidenced by the brushy

fracture. Its toughness was demonstrated by driving a 5 mm diameter rod through the

10   walls of the flat panel without fracturing the panel.

This example demonstrates that a chemical vapor deposition prepared

composite exhibits tough or "brushy failure" but a significantly higher permeability

than the composites of the invention.

15   **Example 7**

A composite U-Bend tube construction was prepared by stretching two 14.7 cm

(5 inch) diameter braids made from alumina fibers (available under the trade

designation "NEXTEL 312"), using 900 denier 1/2 yarn on a 144 carrier braider, 4.1

pick/inch, 0.083 g/cm^2 onto a U-Bend mandrel as described in U.S. Pat. No 5,350,139

20   (Leyderman). The double layer of braids weighed approximately 0.19 g/cm^2. A

phenolic resin emulsion, prepared by mixing one part by volume of phenolic resin

("BKUA-2370") with 5 parts distilled water was brushed onto the braid to produce an

approximately 8 wt-% add-on after the braid had been heated to 200°C in a forced air

oven (available from Despatch Industries, Minneapolis, MN) for approximately 15

25   minutes. The impregnated braid was removed from the U-Bend mandrel and a thin

coating (less than 2% of the total weight of the resin and braid) of the ceramic precursor

slurry described above was brushed onto the binder impregnated braids. The resulting

construction was heated to 1000°C at a heating rate of 100°C/hour in a nitrogen

atmosphere in a furnace (available from CM Corp., Elizabeth, NJ), and then held at that

30   temperature for 15 minutes to form a pyrolyzed preform. The pyrolyzed preform was

then dipped into the ceramic precursor slurry, dried in air, redipped, dried, and then

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cured at 200°C for 15 minutes, followed by heating to 1000°C at a heating rate of 100°C/hour in a nitrogen atmosphere, and then held at that temperature for 10 minutes as described in Example 1. The matrix add-on after firing was approximately 0.9 times the weight of the preform (i.e., the fabric with carbonaceous material thereon). The

5   matrix application was repeated a second time to produce a cumulative matrix add-on of approximately 1.6 times the weight of the preform after firing.

A final sealing coating of a polyureasilazane (obtained under the trade designation "CERASET SN" from Lanxide Corp., Newark, DE) without particles dispersed therein was brushed onto the U-tube assembly followed by firing in a

10   nitrogen atmosphere heating at a rate of 200°C/hour and holding at 1000°C for 15 · minutes to produce a composite containing 0.32 g/cm^2 SiC matrix.

The strength of the U-tube composite was determined using an O-Ring crush test. Rings (2.5 cm in width) were cut from the straight segments of the U-tube and the rings compressed using a Model 1125 tensile testing machine (available from Instron

15   Corp., Canton MA) equipped with a 227 kg (500 lb) load cell and operating at a cross head speed of 0.051 cm/minute (0.02 inches/min). Results of the test are reported in Table 1, below. The U-tube was tough and resistant to fracture as evidenced by the brushy fracture. Its toughness was further demonstrated by driving a 5 mm diameter rod through the walls of the U-tube without fracturing the tubes.

20   The gas permeability for this construction was determined by pressurizing the U-tube to 124 Pascals (0.018 psi) and monitoring the pressure drop across the composite material of the U-tube. The results are reported in Table 1, below.

Comparative Example C-4

25   A composite U-Bend tube construction was prepared by stretching two 14.7 cm (5 inch) diameter braids made from aluminaborosilicate fibers ("NEXTEL 312"), using 900 denier 1/2 yarn on a 144 carrier braider, 4.1 pick/inch, 0.083 gm/cm^2 onto a U-Bend mandrel as described in U.S. Pat. No. 5,350,139 (Leyderman). A phenolic resin emulsion, prepared by mixing one part by volume of phenolic resin ("BKUA-2370")

30   with 5 parts distilled water, was brushed onto the braid to produce an approximately 8 wt-% add-on after the braid had been heated to 200°C in the forced air oven for

26

approximately 15 minutes. The impregnated braid was removed from the mandrel and

placed in a vacuum chemical vapor deposition reactor that was evacuated (10 torr) and

partially refilled with nitrogen (300 torr), followed by heating in nitrogen at a rate of

300°C/hour and held at 1000°C for 30 minutes to pyrolyze the phenolic resin. A SiC

5   matrix was subsequently deposited onto the U-tube from a mixture of hydrogen and

methyl trichlorosilane as described in Example 1 of U.S. Pat. No. 4,397,901 (Warren)

to produce composites containing 0.41 gm/cm^2 of SiC matrix. Permeability and O-

Ring compressive strength data for this construction are reported in Table 1, below.

10

TABLE 1

Composite Permeability

Example	Braid Wt. (g/cm^2)	Matrix Wt. (g/cm^2)	O-Ring Compression Maximum (MPa)	Permeability at 124 Pascal (liters/hr cm^2)
5	0.19	0.32	-	$<14.9 \times 10^{-4}$
6	0.20	0.28	-	$<14.9 \times 10^{-4}$
C-3	0.20	0.34	-	$4,249 \times 10^{-4}$
7	0.19	0.32	11.7	8.76×10^{-4}
C-4	0.19	0.39-0.46	11.3	$>352 \times 10^{-4}$

15   A comparison of the O-ring compressive strength and permeability data for the

samples of Example 7 and Comparative Example C-4 shows that a U-tube construction

based on chemical vapor deposition of the SiC matrix and a U-tube construction based

on composites of the present invention exhibited comparable compression strengths.

Although Example 7 has a sealing coating whereas Comparative Examples C-3 and C-4

20   do not, Examples 5 and 6 do not include the sealing coating, showing that composite

materials according to the present invention have significantly lower permeability.

            Various modifications and alterations to this invention will become apparent to

those skilled in the art without departing from the scope and spirit of this invention. It

25   should be understood that this invention is not intended to be unduly limited by the

illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only. The scope of the invention is intended to be limited only by the claims set forth herein as follows.

What Is Claimed Is:

1. A ceramic composite material comprising:

a ceramic matrix comprising ceramic particles dispersed within a ceramic

bonding phase; and

a plurality of ceramic fiber bundles, each comprising a plurality of continuous

ceramic fibers;

wherein said ceramic matrix does not completely infiltrate a majority of the individual

fiber bundles, and wherein said ceramic particles have at least one fraction of particles

with a median particle size at least as large as the diameter of the largest individual

fibers.

2. The ceramic composite material of claim 1 having a permeability of less

than about 20×10^{-4} l/h·cm^2.

3. The ceramic composite material of claim 2 having a permeability of less

than about 10×10^{-4} l/h·cm^2.

4. The ceramic composite material of claim 1 having a fracture toughness

of at least about 3 MPam$^{1/2}$.

5. The ceramic composite material of claim 4 having a fracture toughness

of at least about 5 MPam$^{1/2}$.

6. The ceramic composite material of claim 1 having a density of at least

about 1.7 g/cm^3.

7. The ceramic composite material of claim 6 having a density of no greater

than about 2.5 g/cm^3.

8.   The ceramic composite material of claim 1 wherein said ceramic

particles comprise a coarse fraction having a median particle size at least as large as the

diameter of the largest individual fibers and a fine fraction having a median particle size

at least 20% less than the median particle size of the coarse fraction.

5

9.   The ceramic composite material of claim 8 wherein said coarse particle

fraction is present in a greater amount than the fine particle fraction.

10.   The ceramic composite material of claim 1 wherein said ceramic fibers

10   include ceramic oxide fibers.

11.   The ceramic composite material of claim 10 wherein said ceramic fibers

include at least one of alumina fibers, aluminosilicate fibers, aluminoborosilicate fibers,

zirconia fibers, yttria-alumina fibers, silicon carbide fibers, and silicon nitride fibers.

15

12.   The ceramic composite material of claim 11 wherein said ceramic oxide

fibers include at least one of aluminosilicate fibers, aluminoborosilicate fibers, or

alumina fibers.

20   13.   The ceramic composite material of claim 1 wherein said fibers include a

carbonaceous coating thereon.

14.   The ceramic composite material of claim 1 wherein said ceramic

particles include at least one of ceramic oxide particles, ceramic carbide particles, and

25   ceramic nitride particles.

15.   The ceramic composite material of claim 14 wherein said ceramic oxide

particles include at least one of alumina particles, zirconia particles, yttria particles,

mullite particles, hafnia, and silica particles.

30

16.   The ceramic composite material of claim 1 wherein said ceramic bonding phase comprises a non-oxide ceramic.

17.   The ceramic composite material of claim 16 wherein said ceramic bonding phase comprises a silicon-containing non-oxide.

18.   The ceramic composite material of claim 17 wherein said silicon-containing non-oxide comprises silicon carbide.

19.   A ceramic composite material consisting essentially of:

a ceramic matrix comprising ceramic particles dispersed within a ceramic bonding phase; and

a plurality of ceramic fiber bundles, each comprising a plurality of continuous ceramic fibers;

wherein said ceramic matrix does not completely infiltrate the individual fiber bundles, and wherein said ceramic particles have at least one fraction of particles with a median particle size at least as large as the diameter of the largest individual fibers.

20.   A ceramic composite material comprising:

a ceramic matrix comprising ceramic particles dispersed within a silicon-containing non-oxide ceramic bonding phase; and

a plurality of ceramic fiber bundles, each comprising a plurality of continuous ceramic oxide fibers;

wherein said ceramic matrix does not completely infiltrate the individual fiber bundles, and wherein said ceramic particles comprise a coarse fraction having a median particle size at least as large as the diameter of the largest individual fibers and a fine fraction having a median particle size at least 20% less than the median particle size of the coarse fraction.

21.   A U-tube comprising ceramic composite material comprising:

a ceramic matrix comprising ceramic particles dispersed within a ceramic

bonding phase; and

a plurality of ceramic fiber bundles, each comprising a plurality of continuous

ceramic fibers;

5   wherein said ceramic matrix does not completely infiltrate a majority of the individual

fiber bundles, and wherein said ceramic particles have at least one fraction of particles

with a median particle size at least as large as the diameter of the largest individual

fibers.

10   22.   The U-tube of claim 21 wherein said ceramic composite material has a

permeability of less than about 20 x 10^{-4} l/h·cm^2.

23.   The U-tube of claim 22 wherein said ceramic composite material has a

permeability of less than about 10 x 10^{-4} l/h·cm^2.

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24.   The U-tube of claim 21 wherein said ceramic composite material has a

fracture toughness of at least about 3 MPam$^{1/2}$.

25.   The U-tube of claim 21 wherein said ceramic particles comprise a coarse

20   fraction having a median particle size at least as large as the diameter of the largest

individual fibers and a fine fraction having a median particle size at least 20% less than

the median particle size of the coarse fraction.

26.   The U-tube of claim 25 wherein said coarse particle fraction is present in

25   a greater amount than the fine particle fraction.

27.   The U-tube of claim 21 wherein said ceramic fibers include at least one

of alumina fibers, aluminosilicate fibers, aluminoborosilicate fibers, zirconia fibers,

yttria-alumina fibers, silicon carbide fibers, and silicon nitride fibers.

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28.   The U-tube of claim 21 wherein said fibers include a carbonaceous coating thereon.

29.   The U-tube of claim 21 wherein said ceramic particles include at least one of ceramic oxide particles, ceramic carbide particles, and ceramic nitride particles.

30.   The U-tube of claim 21 wherein said ceramic bonding phase comprises a non-oxide ceramic.

31.   The U-tube of claim 30 wherein said ceramic bonding phase comprises a silicon-containing non-oxide.

32.   The U-tube of claim 31 wherein said silicon-containing non-oxide comprises silicon carbide.

33.   A method of making a ceramic composite material comprising:
       providing fabric comprising a plurality of ceramic fiber bundles, each bundle comprising a plurality of continuous ceramic fibers;
       providing a slurry comprising ceramic particles dispersed within a preceramic polymer; wherein said ceramic particles have at least one fraction of particles with a median particle size at least as large as the diameter of the largest individual fibers;
       coating said slurry on the fabric; and
       firing the slurry-coated fabric to provide a ceramic matrix that does not completely infiltrate a majority of the individual fiber bundles.

34.   The method of claim 33 wherein said ceramic particles comprise a coarse fraction having a median particle size at least as large as the diameter of the largest individual fibers and a fine fraction having a median particle size at least 20% less than the median particle size of the coarse fraction.

35.   The method of claim 34 wherein said coarse particle fraction is present in a greater amount than said fine particle fraction.

36.   The method of claim 34 wherein prior to the step of coating the slurry on the fabric, the method further comprises:

    forming the fabric into a desired shape;

    coating the fabric with a carbon-containing resin capable of being pyrolyzed to form a carbonaceous layer; and

    pyrolyzing the carbon-containing resin to form a shaped fabric.

37.   The method of claim 36 wherein the step of coating the fabric with the carbon-containing resin is performed prior to the step of forming the fabric.

38.   The method of claim 36 wherein the carbon-containing resin comprises a phenolic resin.

39.   The method of claim 38 wherein the preceramic polymer comprises a silicon-containing polymer.

40.   The method of claim 39 wherein the silicon-containing polymer includes at least one of a polyureasilazane, a polycarbosilane, a polyhydridosiloxane, or a vinylic polysilane.

41.   The method of claim 40 wherein the steps of coating said slurry on the fabric and firing the slurry-coated fabric are repeated at least once.

42.   The method of claim 40 further comprising:

    coating a second preceramic polymer without ceramic particles dispersed therein on the ceramic composite material; and

    firing the polymer-coated fabric to provide a ceramic matrix that does not completely infiltrate a majority of the individual fiber bundles.

43.   A ceramic composite material comprising:

a ceramic matrix comprising ceramic particles dispersed within a ceramic bonding phase; and

fabric comprising at least one ceramic fiber bundle comprising a plurality of continuous ceramic fibers;

wherein said ceramic matrix is in direct contact with less than 70% of the fibers, and wherein said ceramic particles have at least one fraction of particles with a median particle size at least as large as the diameter of the largest individual fibers.

44.   The ceramic composite material of claim 43 which is in the form of a U-shaped tube.

45.   A method of making a ceramic composite material comprising:

providing fabric comprising at least one ceramic fiber bundle comprising a plurality of continuous ceramic fibers;

providing a slurry comprising ceramic particles dispersed within a preceramic polymer; wherein said ceramic particles have at least one fraction of particles with a median particle size at least as large as the diameter of the largest individual fibers;

coating said slurry on the fabric; and

firing the slurry-coated fabric to provide a ceramic matrix that is in direct contact with less than 70% of the fibers.
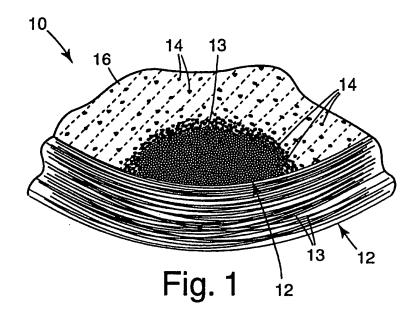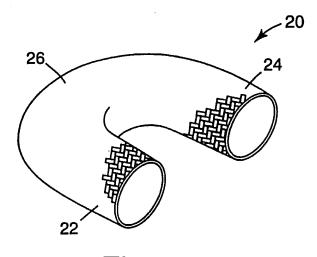
Fig. 1

Fig. 2